

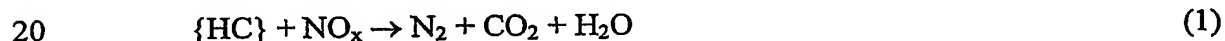
**CATALYST STRUCTURE COMPRISING LEAN NO<sub>x</sub> CATALYST  
COMPOSITION**

5           This invention relates to a catalyst structure for treating exhaust gas of a lean burn internal combustion engine comprising a lean NO<sub>x</sub> catalyst (LNC) composition. In particular, the invention concerns a catalyst structure wherein the LNC composition is selected from the group consisting of: (a) silver or a silver compound supported on alumina; and (b) at least one metal selected from the group consisting of copper (Cu),  
10   iron (Fe), cobalt (Co) and cerium (Ce) supported on at least one zeolite.

LNCs are sometimes also referred to in the literature as non-selective catalytic reduction (NSCR) catalysts, hydrocarbon selective catalytic reduction (HC-SCR) catalysts, lean NO<sub>x</sub> reduction catalysts, "DeNO<sub>x</sub> catalysts" and NO<sub>x</sub> occluding catalysts.

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In lean NO<sub>x</sub> catalysis, hydrocarbons (HC) react with nitrogen oxides (NO<sub>x</sub>), rather than oxygen (O<sub>2</sub>), to form nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) according to reaction (1):



The competitive, non-selective reaction with oxygen is given by reaction (2):



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A number of catalysts are known for selectively promoting the reaction (1) including platinum (Pt) on alumina (Al<sub>2</sub>O<sub>3</sub>), copper (Cu)-substituted zeolite such as Cu/ZSM-5 and silver (Ag) supported on Al<sub>2</sub>O<sub>3</sub> (see e.g. EP 0658368).

30           Pt/Al<sub>2</sub>O<sub>3</sub> is active in a relatively narrow temperature window at relatively low temperature (peak activity ~250°C). Another problem is that it is relatively unselective for N<sub>2</sub> formation in that it favours the formation of N<sub>2</sub>O over N<sub>2</sub> at relatively low temperatures. N<sub>2</sub>O is a potent greenhouse gas (at least 200 times more potent than CO<sub>2</sub>) and accordingly its release into the atmosphere is undesirable.

Zeolite-based LNCs, such as Cu/ZSM5, and Ag/Al<sub>2</sub>O<sub>3</sub> LNCs have wider temperature windows of activity than Pt-based LNCs and also operate at higher temperatures (peak activity of about 400-450°C and above).

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It would be desirable to develop an exhaust system for treating exhaust gas of a lean burn internal combustion engine for selectively reducing NO<sub>x</sub> to N<sub>2</sub> in the presence of a suitable reductant over a relatively broad temperature window of activity without producing N<sub>2</sub>O.

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We have investigated the known silver- and zeolite-based LNCs and we have found that their low temperature activity is improved when the reductant is treated with a partial oxidation catalyst. We believe that this step produces an oxygenated hydrocarbon feedstock. Furthermore, we believe that the activity of Ag/Al<sub>2</sub>O<sub>3</sub> is suppressed by coke formation, which may be one reason why it has not found wider acceptance in the industry. We have now discovered that selective, low temperature NO<sub>x</sub> reduction can be improved by combining known silver- and/or zeolite-based LNCs with at least one partial oxidation catalyst (POC).

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A partial oxidation catalyst (POC) is a catalyst that promotes the partial oxidation of hydrocarbons in exhaust gas of a lean-burn internal combustion engine to carbon monoxide (CO), hydrogen gas (H<sub>2</sub>) and partially oxygenated hydrocarbon species, as opposed to complete oxidation to H<sub>2</sub>O and CO<sub>2</sub>.

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EP 1008379 describes a method and device for treating NO<sub>x</sub> in an internal combustion engine exhaust system comprising a POC upstream of a NO<sub>x</sub> trap, wherein hydrocarbons introduced into the exhaust system upstream of the POC are converted to CO and H<sub>2</sub> for regenerating the NO<sub>x</sub> trap.

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EP 0761289 describes an exhaust gas cleaner and method for removing NO<sub>x</sub> by reduction from a lean burn internal combustion engine exhaust gas. According to the disclosure, nitrogen-containing compounds such as alkyl nitrites, ammonia etc. and aldehydes are produced on e.g. Ag/Al<sub>2</sub>O<sub>3</sub> which are subsequently reduced by being brought into contact with a second catalyst of: (a) titania; (b) a titanium component

supported on an inorganic oxide; (c) an inorganic oxide carrying at least one first component selected from the group consisting of copper, nickel, silver, cobalt and compounds thereof and at least one second component selected from the group consisting of titanium, zirconium and compounds thereof and a third component selected from the group consisting of alkali metal elements and rare earth elements; and (d) an inorganic oxide carrying a titanium component and at least one platinum group metal. The technique of non-selective catalytic reduction is specifically distinguished in the background to the disclosure.

According to a first aspect, the invention provides a catalyst structure for treating exhaust gas from a lean burn internal combustion engine, which catalyst structure comprising a substrate monolith comprising a lean NO<sub>x</sub> catalyst (LNC) composition associated with at least one partial oxidation catalyst (POC), wherein the LNC composition is selected from the group consisting of: (a) silver or a silver compound supported on alumina; and (b) at least one metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co) and cerium (Ce) supported on at least one zeolite, and wherein the at least one POC is selected from the group consisting of: (i) a bulk oxide, a bulk composite oxide or a bulk mixed oxide comprising at least one metal selected from the group consisting of manganese (Mn), iron (Fe), cerium (Ce) and praseodymium (Pr); and (ii) at least one of rhodium (Rh) and palladium (Pd) disposed on at least one inorganic oxide support.

It is believed that where the silver is present as a compound thereof, it is present as its oxide. In use, the silver can be present in the form of its carbonate, hydroxide or nitrate by combining with components of the exhaust gas.

An advantage of the present invention is that low temperature NO<sub>x</sub> conversion activity e.g. from 200-350°C is enhanced compared with Ag/Al<sub>2</sub>O<sub>3</sub> *per se* or, for example, Cu/ZSM5 *per se*.

A further advantage of the Ag/Al<sub>2</sub>O<sub>3</sub> embodiment of the invention is that the arrangement reduces or prevents coke formation on the LNC during extended periods at low temperature, improving the overall activity of the LNC.

For the purposes of comparison, we have investigated the catalyst described in JP 2002370031 which contains Ag on mixed oxides (3-40wt.% CeO<sub>2</sub> on alumina) and found it to be inactive as a LNC.

5       The catalyst structure of the present invention can be arranged in a number of configurations, some of which are shown in Figure 10. The configuration can be selected according to the activity required within a desired temperature window. In one embodiment the substrate monolith comprises a physical mixture of the LNC composition and the at least one POC. In another embodiment, the substrate monolith  
10       comprises a layer of the at least one POC on a layer of the LNC composition. Alternatively, the substrate monolith comprises a layer of the LNC composition on a layer of the at least one POC.

15       A suitable silver loading in the LNC composition of group (a) is in the range 0.5 to 10.0 wt.% based on the total weight of the alumina. Any form of alumina can be used, in the present invention, such as alpha-, delta- or theta-alumina. However, we have found that the best performance is obtained when using high surface area gamma-aluminas.

20       In the LNC composition, the at least one zeolite of the LNC composition can be selected from the group consisting of ZSM-5, ZSM-8, ZSM-11, ZSM-12, ZSM-20, mordenite, gamma-zeolite, beta-zeolite, silicalite, X zeolite, Y zeolite, L zeolite, erionite, USY zeolite or any mixture of two or more thereof.

25       The total amount of the at least one metal selected from the group consisting of Cu, Fe, Co and Ce in the LNC composition of group (b) is suitably in the range 0.5 to 10.0 wt.% based on the total weight of the zeolite.

30       Referring to the at least one POC, the oxides of group (i) can comprise at least one stabiliser selected from the group consisting of: zirconium (Zr), lanthanum (La), aluminium (Al), yttrium (Y), Pr and neodymium (Nd). The at least one metal can form composite oxides or mixed oxides with the stabiliser. Suitable molar ratios of the at least one metal to the at least one stabiliser (in total) is 2:98M to 90:10M, where M is the at least one metal selected from the group consisting of Mn, Fe, Ce and Pr.

“Composite oxide” as defined herein means a largely amorphous oxide material comprising oxides of at least two elements which are not true mixed oxides consisting of the at least two elements.

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A preferable POC of group (i) for use in the invention consists of bulk  $\text{CeO}_2$ , or a mixed oxide or composite oxide of Ce and Zr.

10 The at least one inorganic oxide support of the POC of group (ii) can comprise an oxide of Al, Ce, Zr, titanium (Ti), silicon (Si), magnesium (Mg), chromium (Cr) or a mixture, composite oxide or mixed oxide of any two or more thereof, such as a mixed oxide or a composite oxide of Ce and Zr.

15 In other embodiments, the composite oxide or mixed oxide comprises a zeolite, a non-zeolite silica-alumina, a silica-zirconia, an alumina-zirconia, an alumina-chromia, an alumina-ceria or a ceria-titania.

20 A suitable total loading of the Rh and/or Pd in the at least one POC of group (ii) is in the range 0.5 to 10.0 wt.% of Rh and/or Pd, based on the total weight of the at least one support.

25 The or each POC oxide of group (i) and/or the or each POC support of group (ii) can be doped with at least one of lanthanum (La), barium (Ba), Ce, tungsten (W), Si and Mn to improve the stability of the support to high temperature ageing, act as a lean  $\text{NO}_x$  promoter and/or improve the oxygen storage capacity of the system, the latter particularly in the case of manganese. Tungsten is a particularly suitable dopant for improving the thermal stability of group (ii) supports such as alumina or titania.

30 Suitable values of dopant addition are from 0.5 to 20wt%.

Typical weight ratios of the LNC composition to the at least one POC are in the range 20:1 to 1:5, optionally from 10:1 to 1:1.

Methods of preparing the LNC compositions according to the invention are known and include wet impregnation, ion-exchange and co-precipitation. A detailed discussion of which methods will not be made here, as the skilled person is aware of such techniques.

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According to a second aspect, the invention provides an exhaust system for a lean-burn internal combustion engine comprising a catalyst structure according to the invention.

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The catalyst structure of the present invention can be configured in a number of ways, the activity of some of which are shown in the accompanying Examples and Figures. In one embodiment, some or all of the LNC composition on the substrate monolith is located downstream of the at least one POC. In another embodiment, some or all of the LNC composition is located on a separate substrate monolith disposed downstream of the substrate monolith comprising the at least one POC.

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In an alternative embodiment, some of the LNC composition on the substrate monolith is located upstream of the at least one POC. In another embodiment, some of the LNC composition is located on a separate substrate monolith disposed upstream of the substrate monolith comprising the at least one POC.

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According to a third aspect according to the invention, an apparatus comprises a lean-burn internal combustion engine including an exhaust system according to the invention.

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The exhaust system can comprise means for introducing a reductant into an exhaust gas upstream of the LNC composition. Embodiments of the exhaust system wherein at least one POC is upstream of the LNC composition can optionally include an additional means for introducing a reductant into an exhaust gas upstream of at least one POC. A reason for this is that in certain embodiments, e.g. wherein the POC is  $\text{CeO}_2$ , the POC tends to combust hydrocarbons completely at higher temperatures, hence  $\text{NO}_x$  conversion is reduced on the downstream LNC composition because of lack of reductant. A second injector between the at least one POC bed and the LNC composition bed can be used to inject hydrocarbon reductant over the LNC at temperatures which are too high

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for partial oxidation on the upstream at least one POC. In the case of  $\text{CeO}_2$ , a suitable temperature for injection of hydrocarbon between the at least one POC and downstream LNC composition is above about  $350^\circ\text{C}$ .

5           Alternatively, a lower loading of  $\text{CeO}_2$ , or a shorter length (or thinner "stripe") of the at least one POC, can be disposed on the substrate monolith upstream of the LNC composition to increase the amount of hydrocarbon slip or breakthrough to the downstream LNC composition.

10           The means for introducing a reductant into an exhaust gas upstream of the LNC composition can comprise at least one of: means for injecting the reductant into the exhaust gas; means for adjusting the ignition timing of at least one engine cylinder; and means for adjusting the engine air-to-fuel ratio.

15           Typically, a source of hydrocarbon reductant comprises the fuel that powers the engine.

          The apparatus can comprise means for controlling the or each reductant introducing means. In one embodiment, the control means is arranged, when in use, to  
20   introduce the reductant into the exhaust gas when the POC is from between  $200\text{--}350^\circ\text{C}$  in temperature, such as in the case where the POC is  $\text{CeO}_2$  and is located upstream of the LNC composition. This arrangement can reduce or prevent complete combustion of hydrocarbon upstream of the LNC composition, to the detriment of higher temperature  $\text{NO}_x$  reduction.

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          Generally, the control means can be arranged, when in use, to introduce the reductant into the exhaust gas when the LNC composition is above  $200^\circ\text{C}$  in temperature.

30           Typically, the control means can include a pre-programmed electronic control unit incorporating a processor and can form part of the engine control unit, for example. The exhaust system can include sensor means for inputting signals, such as bed temperature, tailpipe  $\text{NO}_x$  composition and  $\text{NO}_x$  content of the inlet gas, in order to

regulate hydrocarbon injection, with the overall effect being to maintain a desired NO<sub>x</sub> conversion in the system.

The engine of the apparatus according to the invention is typically a diesel engine, optionally a heavy-duty diesel engine, but it can be any engine producing lambda > 1 exhaust gas e.g. a lean-burn gasoline engine or an engine powered by compressed natural gas (CNG) or liquid petroleum gas (LPG).

A suitable substrate monolith for use in the present invention can be a flow-through monolith of metal or ceramic construction. Where ceramic, the substrate can be cordierite or silicon carbide, for example. Alternatively, the catalyst structure can include a filter substrate such as a wall-flow filter.

According to fourth aspect, the invention provides a method of selectively reducing NO<sub>x</sub> in an exhaust gas of a lean burn internal combustion engine to N<sub>2</sub>, which method comprising introducing a reductant into the exhaust gas and contacting the resulting mixture with a lean NO<sub>x</sub> catalyst (LNC) composition associated with at least one partial oxidation catalyst (POC), wherein the LNC composition is selected from the group consisting of: (a) silver or a silver compound supported on alumina; and (b) at least one metal selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co) and cerium (Ce) supported on at least one zeolite, and wherein the at least one POC is selected from the group consisting of: (i) a bulk oxide, a bulk composite oxide or a bulk mixed oxide comprising at least one metal selected from the group consisting of manganese (Mn), iron (Fe), cerium (Ce) and praseodymium (Pr); and (ii) at least one of rhodium (Rh) and palladium (Pd) disposed on at least one inorganic oxide support.

If desired, the catalyst structure of the present invention can be combined with one or more additional LNCs to yield an exhaust system with yet further improved activity across a desired temperature window. In practical applications it may be desirable to include an oxidation catalyst to remove excess reductant which slips the LNC composition.



In order that the invention may be more fully understood, the following Examples are provided by way of illustration only and with reference to the accompanying drawings, in which:

5        Figure 1 is a graph comparing %NO<sub>x</sub> conversion between steady state and transient modes for Comparative Example 1 as a function of temperature;

10        Figure 2 is a graph showing %NO<sub>x</sub> conversion over the Catalyst of Example 1 compared with the Catalyst of Comparative Example 2 in the steady state mode as a function of temperature;

15        Figure 3 is a graph showing the outlet NO<sub>x</sub> concentration as a function of time at 200°C, 250°C and 300°C over 2%Ag/Al<sub>2</sub>O<sub>3</sub> and the 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> mixture in the steady mode;

20        Figure 4 is a graph showing the effect of ramp down (steady state 15 minutes) and ramp up (steady state 15 minutes) on NO<sub>x</sub> conversion of 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (4:1);

25        Figure 5 is a graph showing the effect of ramp down (steady state 15 minutes) and ramp up (steady state 15 minutes) on HC conversion of 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (4:1);

30        Figure 6 is a graph comparing the effect of ageing on Comparative Example 1 and Example 1 catalysts on NO<sub>x</sub> conversion;

35        Figure 7 is a graph showing %NO<sub>x</sub> conversion as a function of temperature for 5Cu/ZSM5 catalyst structures compared with 5Cu/ZSM5 catalyst *per se*;

40        Figure 8 is a graph showing %NO<sub>x</sub> conversion as a function of temperature for 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst structures compared with 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst *per se*;

45        Figure 9 is a graph showing %NO<sub>x</sub> conversion as a function of temperature for a catalyst according to JP 2002370031 compared with 2Ag/Al<sub>2</sub>O<sub>3</sub> and 5Cu/ZSM5 catalyst structures according to the invention; and

Figure 10A-F includes a series of schematic arrangements of catalyst structures according to the present invention.

Referring to Figure 10, Figure 10A is a schematic diagram representing an exhaust line including a can comprising a catalyst structure according to the invention comprising a ceramic flow-through substrate monolith disposed between two diffusers. "HC" represents a schematic injection point for hydrocarbon reductant. The upstream end zone (as shown by the direction of flow arrows) of the substrate monolith comprises an upper layer of a POC (such as bulk  $\text{CeO}_2$ ) and an underlayer of LNC composition, such as  $\text{Ag}/\text{Al}_2\text{O}_3$ .

In an alternative configuration of the Figure 10A embodiment shown in Figure 10B, the underlayer in the upstream zone is the POC, whereas the overlayer is the LNC.

Figure 10C shows a further alternative to the arrangement shown in Figure 10A, wherein the POC is disposed in an overlayer on the LNC on a first substrate monolith and a second substrate monolith coated with LNC is disposed downstream. An additional injector is disposed between the first and second substrate monoliths and a control means (not shown) is arranged to inject hydrocarbon between the two substrate monoliths e.g. continuously when the downstream LNC is above e.g.  $200^\circ\text{C}$  (when a  $\text{Ag}/\text{Al}_2\text{O}_3$  or  $\text{Cu}/\text{ZSM5}$  catalyst is used) and to inject hydrocarbon upstream of the upstream substrate monolith at, for example,  $200\text{-}350^\circ\text{C}$  in the case of  $\text{CeO}_2$  or Ce-containing mixed- or composite-oxides. This arrangement enables hydrocarbon to contact the downstream LNC at higher temperatures in order to promote  $\text{NO}_x$  reduction, which hydrocarbon would otherwise be combusted on the upstream POC if the exhaust system comprised only an hydrocarbon injector upstream of the POC. Optionally, the Figure 10C arrangement can also include an additional injector between the upstream and downstream zones for similar reasons. The first and second substrate monoliths of Figure 10C can be inserted into the same can or separate cans in the exhaust line.

Alternatively, the LNC can be disposed in a zone on the front (upstream) end of the substrate monolith, and the LNC can be arranged in an overlayer on the POC as shown in Figure 10D.

The length of the zones in each of the embodiments represented in Figure 10 can be selected according to the desired activity of the zones, the active catalyst used e.g. to enable thrifting of catalyst etc. In the arrangement shown in Figure 10E, for example, a short zone or "stripe" of POC is used on the upstream end to limit or "trim" HC combustion in the catalyst structure at higher temperature.

The Figure 10F embodiment shows an arrangement wherein the LNC and POC are coated on the catalyst substrate as a physical mixture or the entire length of the substrate monolith includes an overlayer of POC and an underlayer of LNC or vice versa.

### **Comparative Example 1**

#### **2 wt% Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst Preparation**

An impregnated Ag catalyst at 2wt% Ag based on the weight of the Al<sub>2</sub>O<sub>3</sub> support (referred to hereinafter as 2Ag/Al<sub>2</sub>O<sub>3</sub>) was made using silver nitrate by a wet impregnation method. The silver nitrate was dissolved in the appropriate amount of water measured from the pore volume of an Al<sub>2</sub>O<sub>3</sub> support. The solution was then added to the Al<sub>2</sub>O<sub>3</sub> with mixing. After drying overnight, the sample was calcined in air at 500°C for 2 hours. The resulting catalyst was pelleted and particles in the size range 250<d<355 μm were selected.

### **Comparative Example 2**

#### **Mixed 4:1 2 wt% Ag/Al<sub>2</sub>O<sub>3</sub>:cordierite Catalyst Preparation**

The pelleted catalyst particles in the size range 250<d<355 μm prepared according to Comparative Example 1 were physically mixed with pelleted particles of cordierite of the same size in a weight ratio of 4:1 2Ag/Al<sub>2</sub>O<sub>3</sub>:cordierite.

**Example 1****4:1 2 wt% Ag/Al<sub>2</sub>O<sub>3</sub>:CeO<sub>2</sub> Catalyst Preparation**

5        The pelleted catalyst particles in the size range  $250 < d < 355 \mu\text{m}$  prepared according to Comparative Example 1 were physically mixed with pelleted particles of bulk ceria of the same size in a weight ratio of 4:1 2Ag/Al<sub>2</sub>O<sub>3</sub>:ceria.

**Example 2**

10        **Coated substrate including 2 wt% Ag/Al<sub>2</sub>O<sub>3</sub>**

Three cores from ceramic flow-through monolith substrates were prepared, each 2.54cm (1 inch) in diameter and 7.62 cm (3 inches) in length. A first core was coated with a washcoat containing the powder form of the catalyst of Comparative Example 1.

15        The Ag/Al<sub>2</sub>O<sub>3</sub> loading was 2.5g per cubic inch (152.6g per litre). A second core was coated with a first layer of CeO<sub>2</sub> powder and a second layer (overlayer) of the catalyst of Comparative Example 1 at the same loading as the first core. The catalyst loading of the 2Ag/Al<sub>2</sub>O<sub>3</sub>:CeO<sub>2</sub> was 4:1. In the third core, one end of the core was coated with a first layer of the same amount of CeO<sub>2</sub> powder as the second core to a depth of 2.54 cm (one

20        inch), and a second layer (overlayer) of the catalyst of Comparative Example 1 at the same loading as the first core. The catalyst loading of 2Ag/Al<sub>2</sub>O<sub>3</sub>:CeO<sub>2</sub> on the whole of the third core was 4:1.

**Example 3**

25        **Coated substrate including 5 wt% Cu/ZSM5**

Example 2 was repeated except in that a 5wt% Cu/ZSM5 catalyst prepared by wet impregnation was used instead of the powdered 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst.

30        **Comparative Example 3**

**Coated Substrate including catalyst of JP 2002370031**

A ceramic flow-through monolith substrate core 2.54cm (1 inch) in diameter and 7.62 cm (3 inches) in length was coated with alumina powder at a loading of 2.5 g per

cubic inch (152.6g per litre) and the coated core was dried. The washcoated alumina was then impregnated with a mixture of silver and cerium salts to achieve a final catalyst loading of 2wt% silver and 10wt% cerium, and the resulting piece was dried and calcined. As far as the abstract of this patent publication can be understood, the above  
5 arrangement falls within its teaching.

#### **Example 4**

##### **Activity Measurements**

10 The activity of the pelleted catalysts to reduce NO to N<sub>2</sub> using MK1 (diesel fuel) as the reductant was measured in a simulated catalyst activity test (SCAT) gas rig species. The simulated exhaust gas composition used in the test was as follows: NO 500ppm, C1 2250ppm (MK1 diesel fuel), CO 200ppm, O<sub>2</sub> 9%, H<sub>2</sub>O 4.5%, CO<sub>2</sub> 4.5%, N<sub>2</sub> balance (C1:NO<sub>x</sub> 4.5:1). The data was collected in one of two modes:

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- (i) steady state conditions with 15 minutes dwell at each temperature, (data points collected at the end of 15 minutes); or
- (ii) transient ramp up at 10°C per minute temperature from 200°C to 500°C.

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The coated cores were tested only under steady state conditions (data collection as above) in the following simulated exhaust gas composition: NO 500ppm, C1 2250ppm (US06 diesel fuel), CO 200ppm, O<sub>2</sub> 8%, H<sub>2</sub>O 4.5%, CO<sub>2</sub> 4.5%, N<sub>2</sub> balance (C1:NO<sub>x</sub> 4.5:1).

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#### **Comparative Example 4**

##### **Results of Activity Measurements on Catalyst of Comparative Example 1**

Figure 1 shows a graph comparing %NO<sub>x</sub> conversion between steady state and  
30 transient modes for the catalyst of Comparative Example 1 as a function of temperature. It can be seen that the sample is very active for NO<sub>x</sub> conversion between 300°C and 550°C (~60% conversion) in the transient mode, but it is severely deactivated in the steady state mode compared with the transient mode. We believe that this deactivation is caused by carbon species ("coke") deposited on the catalyst surface after exposure to the

gas mixture for long periods at low temperature. Such conditions can be encountered in the exhaust of a diesel engine. Reasons for the above conclusion include our finding that catalyst deactivation is less severe at a C1:NO<sub>x</sub> ratio of 3:1 and activity is restored by heating the deactivated catalyst in the reaction mixture at 550°C (results not shown).

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### **Example 5**

#### **Results of Activity Measurements on Catalyst of Example 1**

Figure 2 shows the %NO<sub>x</sub> conversion activity over the 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst of Example 1 compared with the 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst of Comparative Example 2 in the steady state mode as a function of temperature. The results show that the addition of particulate CeO<sub>2</sub> to the 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst greatly enhances its activity between 200°C-350°C. We believe that this results from generation of partial oxidation products from the MK1 hydrocarbon in the low temperature region which promote NO<sub>x</sub> reduction on the 2Ag/Al<sub>2</sub>O<sub>3</sub> LNC. The control sample mixed with cordierite has no significant activity in this temperature region. Higher temperature activity is lower with the 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> mixture due to the non-selective HC oxidation over the CeO<sub>2</sub>, but this is dependent on the configuration of the catalyst structure as shown in Example 9 and Figure 8.

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Figure 3 shows the outlet NO<sub>x</sub> concentration (ppm) as a function of time at 200°C, 250°C and 300°C over a 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst of Comparative Example 1 and the 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst of Example 1 in the steady mode. The detectors were switched to measure inlet NO<sub>x</sub> concentration during periods of temperature adjustment. The 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst shows substantially no decay in activity during the 15 minute steady state data collection period at 250°C and 300°C compared with the 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst. We believe that this is due to a combination of: the absence of any coke deposition on the 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst; and the feed stock containing reformed i.e. partially oxidised MK1 hydrocarbon products that are particularly effective for promoting NO<sub>x</sub> reduction. It can be seen that at 200°C, NO<sub>x</sub> conversion tails off over the 2Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, possibly as a result of coking of the catalyst.

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**Example 6****Results of Activity Measurements: Steady State Ramp-Up and Ramp-Down on Catalyst of Example 1**

The activity of the 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst under steady state conditions from 500°C to 200°C and then from 200°C to 500°C (C1:NO<sub>x</sub>=4.5:1) was measured and the results are shown in Figures 4 and 5 respectively, following the procedure illustrated in Figure 3. The NO<sub>x</sub> and HC conversion are similar between ramp down and ramp up and no catalyst deactivation was observed. The effect of lowering the C1:NO<sub>x</sub> ratio to 3:1 is also shown. In contrast to previous results with 2Ag/Al<sub>2</sub>O<sub>3</sub> alone, the NO<sub>x</sub> conversion is lower at low temperature at a C1:NO<sub>x</sub> ratio of 3:1. The results are summarised in Table 1.

**Table 1: Effect of CeO<sub>2</sub> addition on 2Ag/Al<sub>2</sub>O<sub>3</sub> lean NO<sub>x</sub> activity.**

Catalyst	NO <sub>x</sub> conversion			HC conversion		
	200°C	250°C	300°C	200°C	250°C	300°C
2Ag/Al <sub>2</sub> O <sub>3</sub> +corderite	8	7	13	--	--	--
2Ag/Al <sub>2</sub> O <sub>3</sub> - CeO <sub>2</sub>	12	41	37	1	43	56
2Ag/Al <sub>2</sub> O <sub>3</sub> - CeO <sub>2</sub> *	14	24	28	19	56	68

\*C1:NO<sub>x</sub>=3:1

**Example 7****Catalyst Ageing**

The 2Ag/Al<sub>2</sub>O<sub>3</sub> and 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalysts were lean hydrothermally aged in a 10% H<sub>2</sub>O and air mixture at 700°C for 16 hours and the steady state activity of the resulting catalysts are shown in Fig 6. It can be seen that even after the high temperature ageing, the presence of CeO<sub>2</sub> is beneficial to the low temperature activity.

### **Example 8**

#### **Results of Activity Measurements on Catalyst Cores of Example 3**

The results of steady state analysis tests performed on the catalyst cores of Example 3, wherein the third core was oriented with the CeO<sub>2</sub> zone on the upstream side are shown in Figure 7. It can be seen that low temperature NO<sub>x</sub> conversion in the 5Cu/ZSM5 core is improved for the catalyst structures containing CeO<sub>2</sub> relative to 5Cu/ZSM5 *per se*. We believe that this results from the supply of partially oxidised US06 hydrocarbon products to the LNC at low temperature.

### **Example 9**

#### **Results of Activity Measurements on Catalyst Cores of Example 3**

The results of steady state analysis tests performed on the catalyst cores of Example 2 are shown in Figure 7. Two configurations of the third core were tested: the CeO<sub>2</sub> zone on the upstream end; and the CeO<sub>2</sub> zone on the downstream end. It can be seen that low temperature NO<sub>x</sub> conversion in the 2Ag/Al<sub>2</sub>O<sub>3</sub> core is improved for the catalyst structures containing CeO<sub>2</sub> relative to 2Ag/Al<sub>2</sub>O<sub>3</sub> *per se*. We believe that this results from a combination of partial oxidation products in the feedstock contacting the LNC and reduced coking of the LNC. Higher temperature NO<sub>x</sub> conversion is suppressed in the configurations wherein the CeO<sub>2</sub> is present in the upstream zone of the core relative to 2Ag/Al<sub>2</sub>O<sub>3</sub> *per se*, because the CeO<sub>2</sub> favours complete combustion of the hydrocarbon instead of partial oxidation at higher temperatures. However, this can be retained with improved low temperature NO<sub>x</sub> conversion relative to 2Ag/Al<sub>2</sub>O<sub>3</sub> *per se* when the mixed 2Ag/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> zone is on the downstream end of the core with 2Ag/Al<sub>2</sub>O<sub>3</sub> *per se* on the upstream end zone.

### **Comparative Example 4**

#### **Results of Activity Measurements on Catalyst of Comparative Example 3**

The activity of the catalyst of JP 2002370031 tested under steady state conditions is shown in Figure 9, compared to the activity of comparable catalyst arrangements of the 5Cu/ZSM5 and 2Ag/Al<sub>2</sub>O<sub>3</sub> embodiments according to the invention.